Nanoporous Aluminum Oxide Templates of Arbitrary Thickness on Silicon Carrier Wafers

5/30/19

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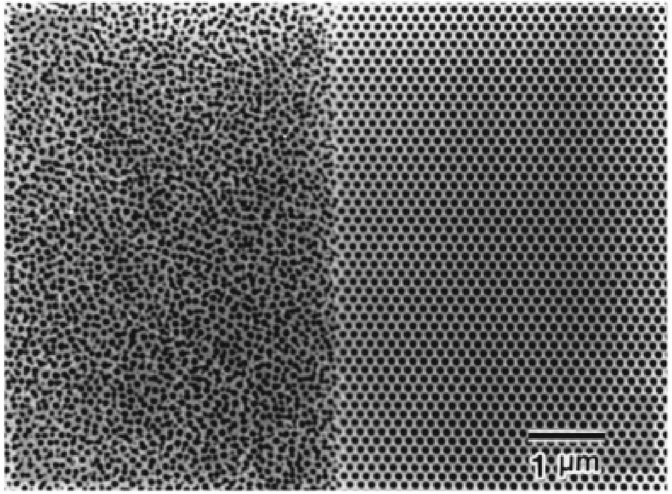
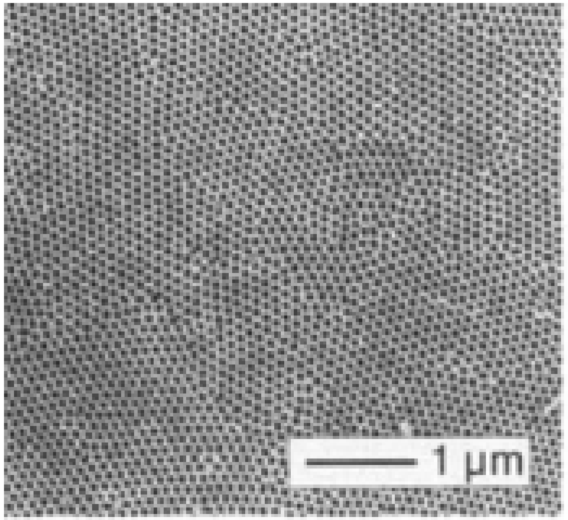
Talk Outline

- Anodized aluminum oxide (AAO)
  - Manufacturing and uses
- AAO on silicon
  - Challenges of thick coatings
- Present work: Solving thick AAO-on-Si challenge using macroscale thermal bonding

Anodized Aluminum Oxide (AAO) - History

- More than 70 years of research
- Physical properties, corrosion resistance, mechanism of formation → nanotechnology
- Ordered AAO has seminal works from the mid to late 1990s from Masuda et al. and Jessensky et al.

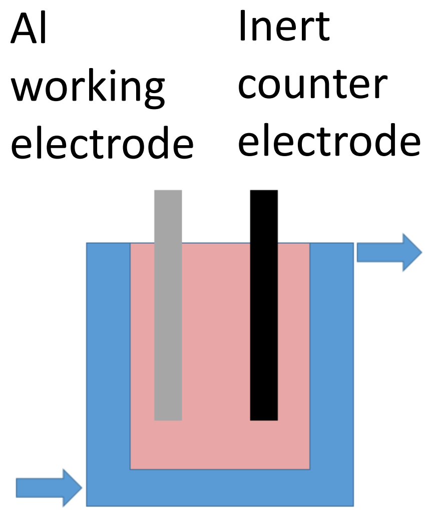




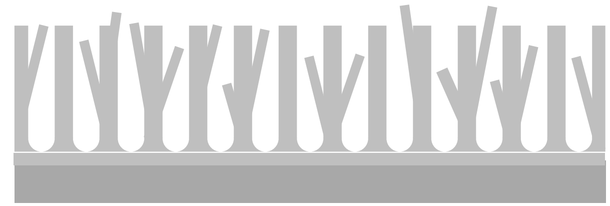
H. Masuda et al., *Appl. Phys. Lett*, **71** (1997)
O. Jessensky, *J. Electrochem. Soc.*, **145** (1998).

Ordered AAO – Two-Step Process

Pure, flat aluminum foil

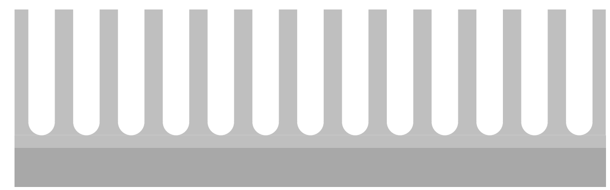


Temperature controlled anodization bath



Disordered aluminum after 1^{st} anodization step

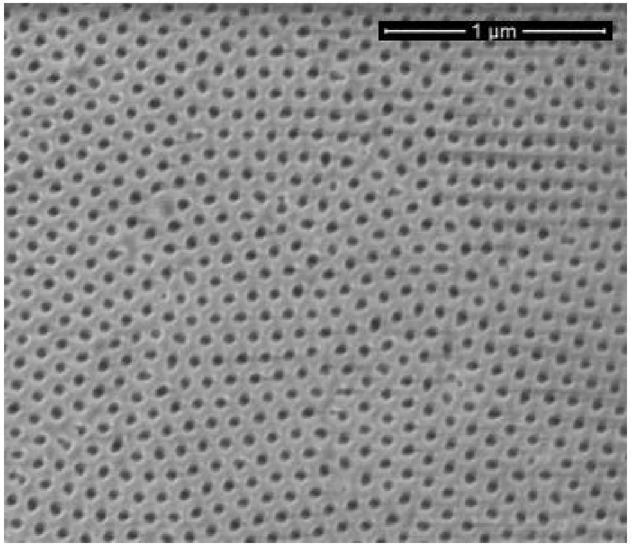
Dimpled aluminum after etching away 1^{st} layer of AAO

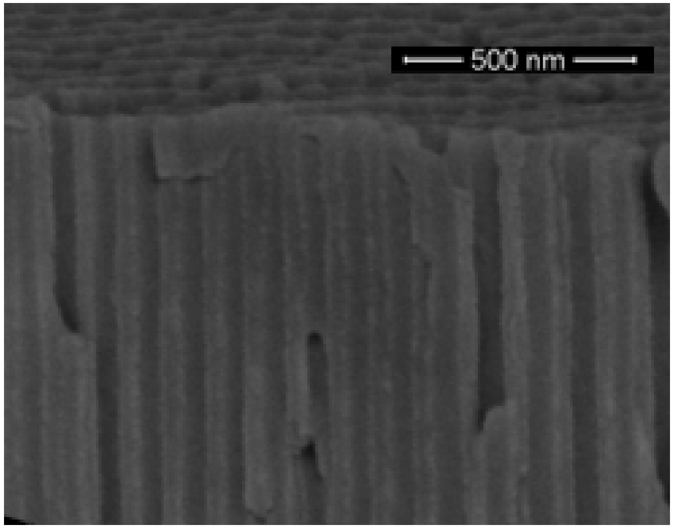


Final well-ordered AAO after 2^{nd} anodization with barrier layer

Anodized Aluminum Oxide (AAO)

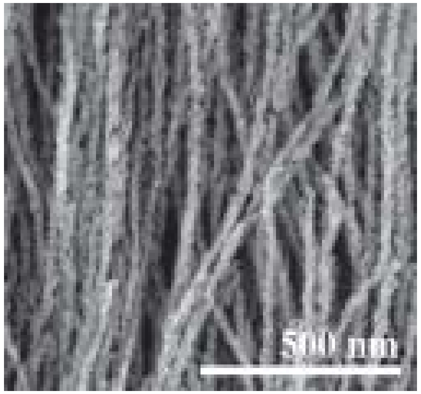
- Highly-ordered, high-aspect ratio, porous layer
- Controllable pore size <20 to >200 nm
- Controllable pore spacing
- Thickness dependent on anodization time



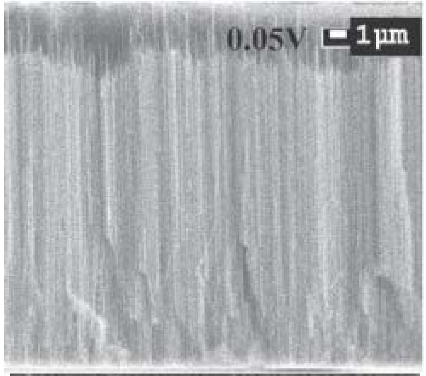


AAO Allows for Templated Nanomanufacturing

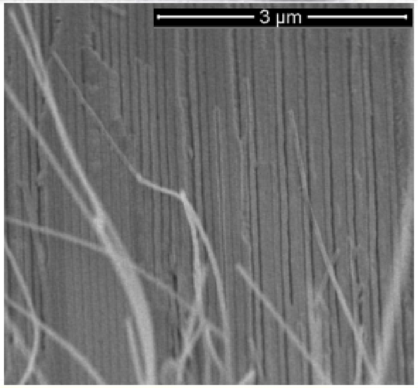
- Pd nanowires for hydrogen sensing[1]



- Bi_2Te_3 for enhanced thermoelectrics[2]



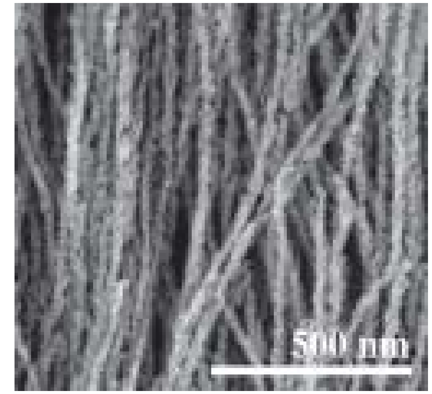
- Carbon nanotubes for supercapacitors

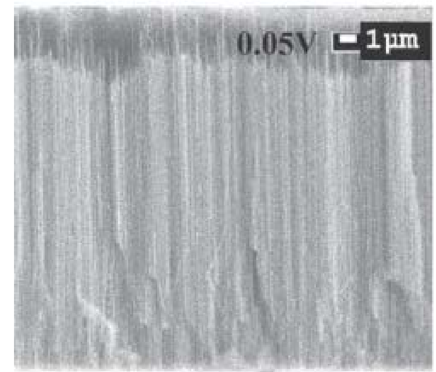


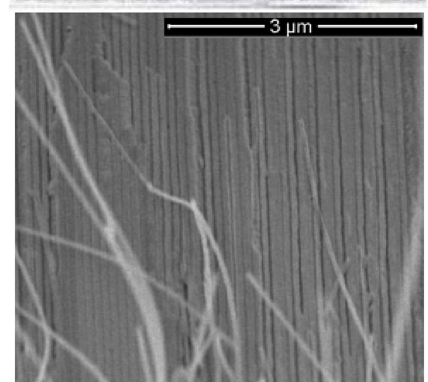
[1]L. Du et al., *ACS Appl. Nano Mater.*, **2**, 1178–1184 (2019)
[2]W. Li et al., *Nanotechnology,* **30** (2019)

AAO on Si Widens Applications of Systems-on-a-Chip

- Pd nanowires for hydrogen sensing[1]
  - All-in-one detection and warning
- Bi_2Te_3 for confined thermoelectrics[2]
  - Efficient heat sink energy scavenging
- Carbon nanotubes for supercapacitors
  - Highly cyclable on-chip power







[1]L. Du et al., *ACS Appl. Nano Mater.*, **2**, 1178–1184 (2019)
[2]W. Li et al., *Nanotechnology,* **30** (2019)

Current Methods of AAO on Si are Limited

- Template transfer[1]
  - Grow AAO on aluminum foil
  - Remove AAO from aluminum through etching/electrochemistry
  - Transfer to new substrate
  - Problem: Scalability
- Film deposition[2]
  - Evaporate/sputter aluminum directly onto substrate
  - Grow AAO on substrate
  - Problem: Only thin films (few micrometers)

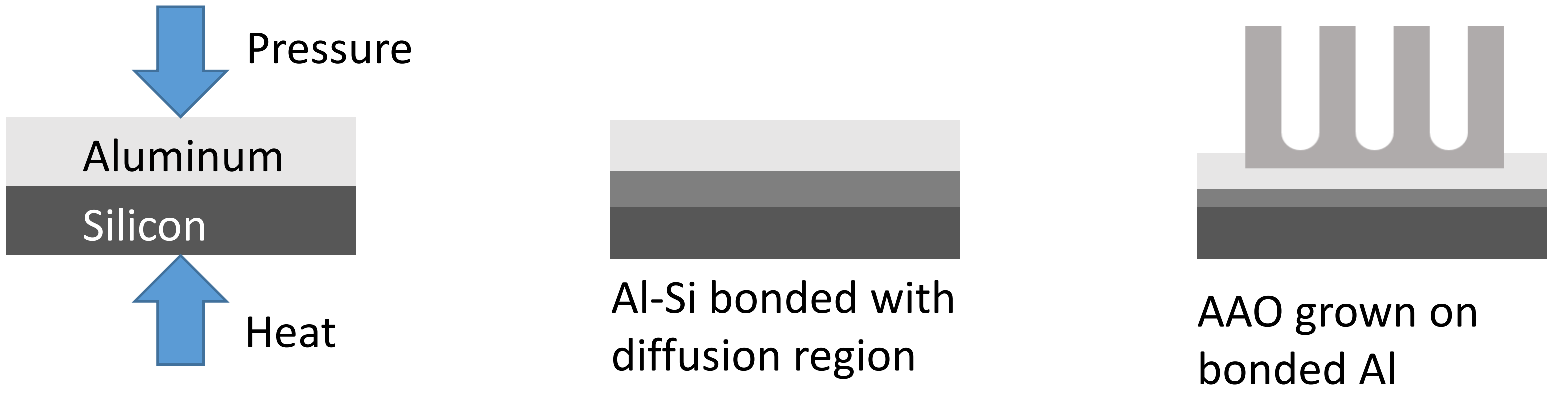
[1]H. Y. Jung et al., *Appl. Phys. Lett.*, **89**, 1–4 (2006)
[2]N. Berger et al., *Appl. Phys. A Mater. Sci. Process.* (2016)

Scalable Thick-Film AAO-on-Si is Desirable

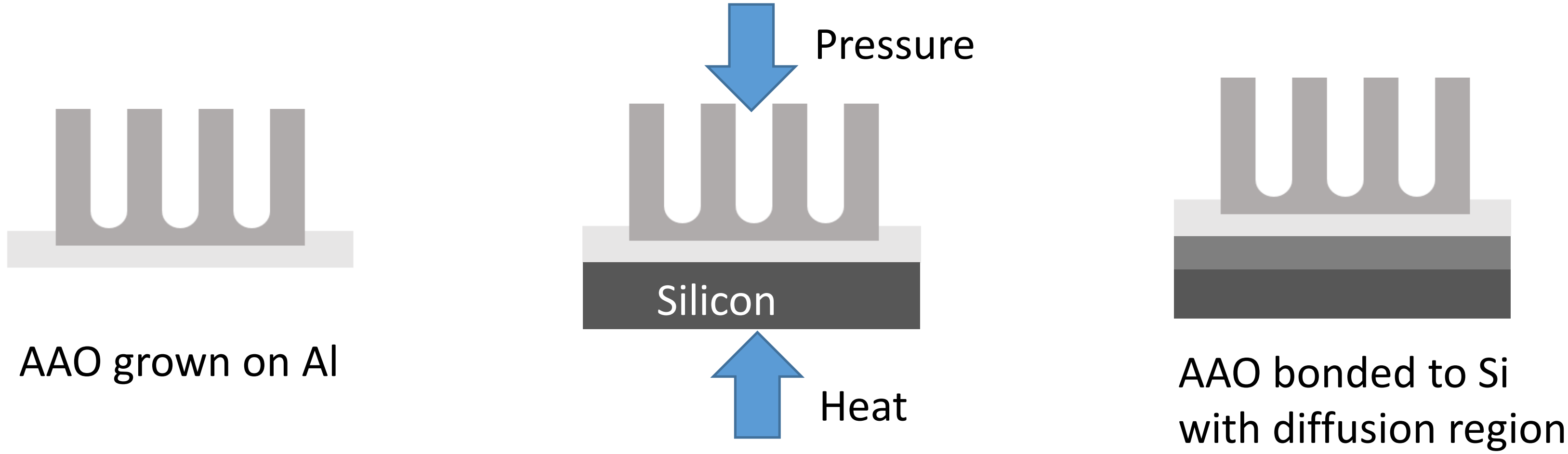
- Thin films limit the performance of technologies which rely on large volume/surface area.
  - Sensors
  - Thermoelectrics
  - Supercapacitors
- Thicker AAO films would allow for greater on-chip sensor sensitivity, energy generation, and energy storage per unit planar area.

Thick AAO on Si: Two Methods

- Al-Si bonding before anodization

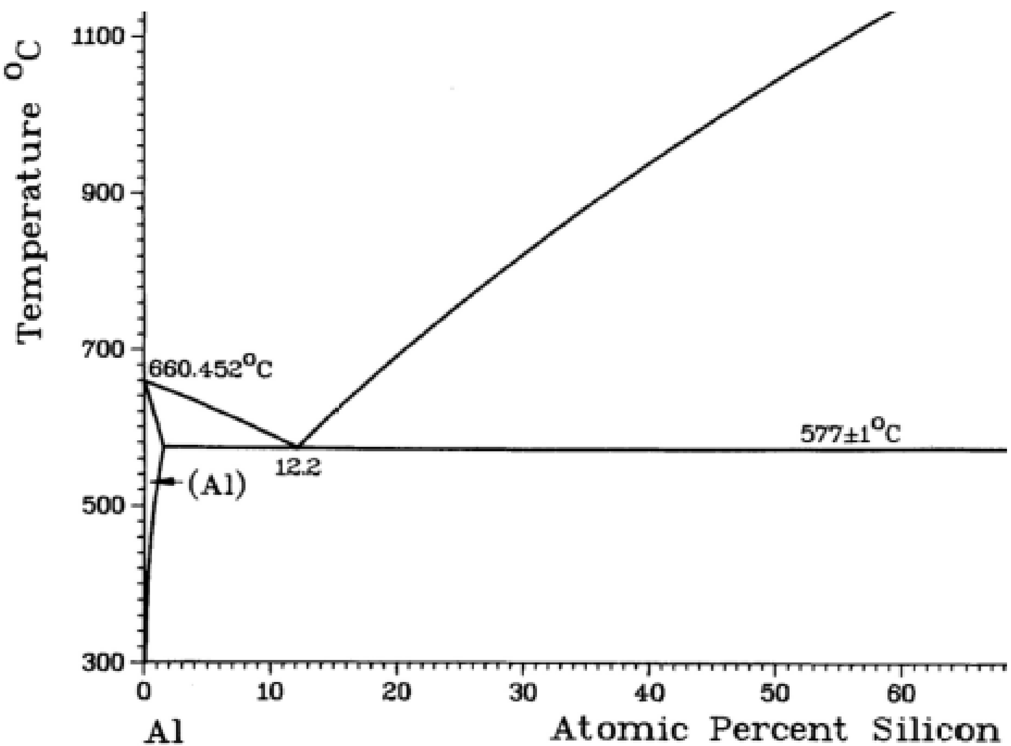


- Al-Si bonding after anodization



Diffusion Bonding of Al and Si

- Temperatures near the AlSi eutectic of 577^{o}C were targeted
- All treatments under flowing argon



Results of Heat Treatments

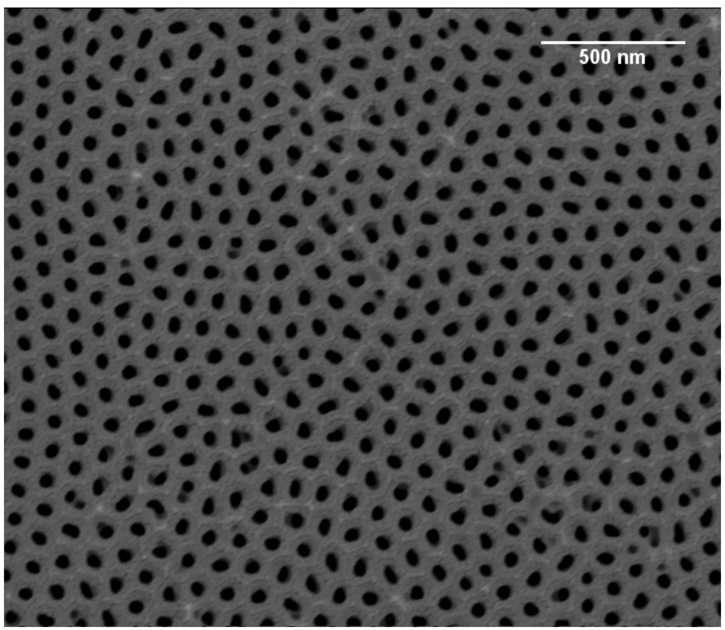
- Temperatures near the AlSi eutectic of 577°C were targeted
- All treatments under flowing argon

Temperature (°C)	Time (min)	Bonding	Pristine Surface
570	5	No	Yes
570	10	No	Yes
570	20	Delicate	Yes
570	40	Delicate	Yes
570	80	Yes	No
580	5	No	Yes
580	10	No	Yes
580	**20**	**Yes**	**Yes**
580	40	Yes	No
580	80	Yes	No

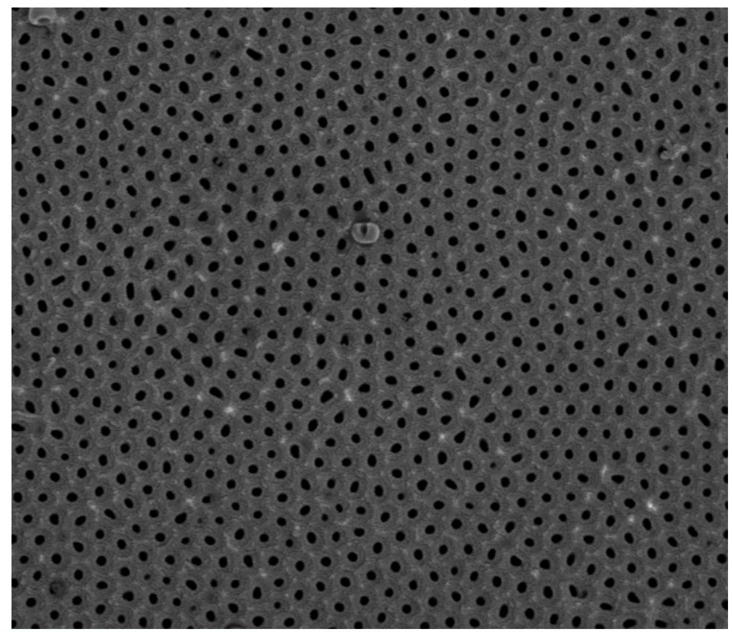
Bonding Before Anodizing Maintains Ordering and Decreases Pore Diameter

- 2nd anodization: 40 V, 0.3 M Oxalic Acid, 15°C

- Bulk Al
  - Avg Dp: 51 nm



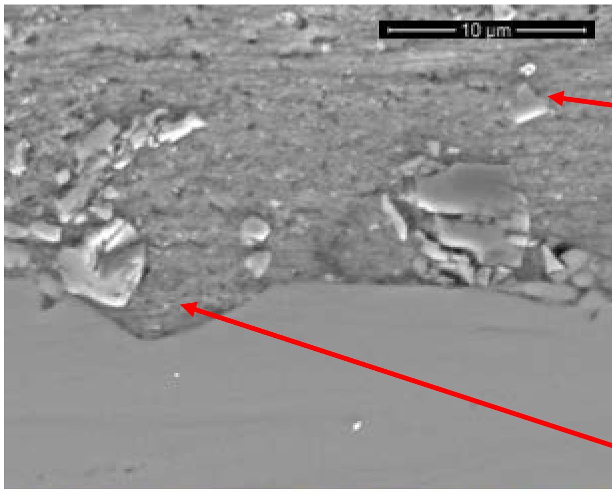
- Bonded Al
  - Avg Dp: 34 nm

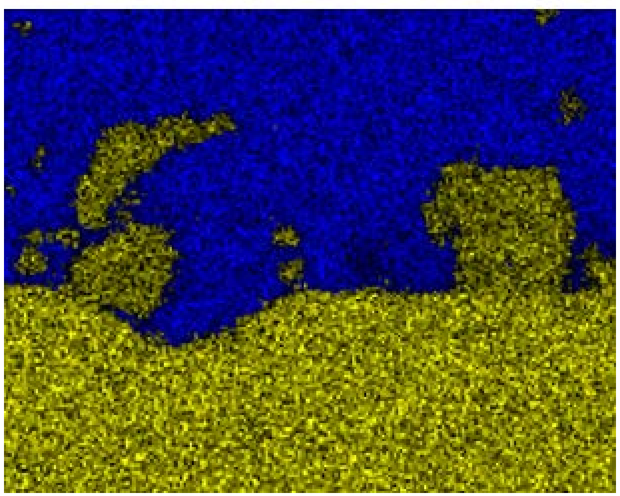


Eutectic Reaction at Al-Si Interface

Aluminum

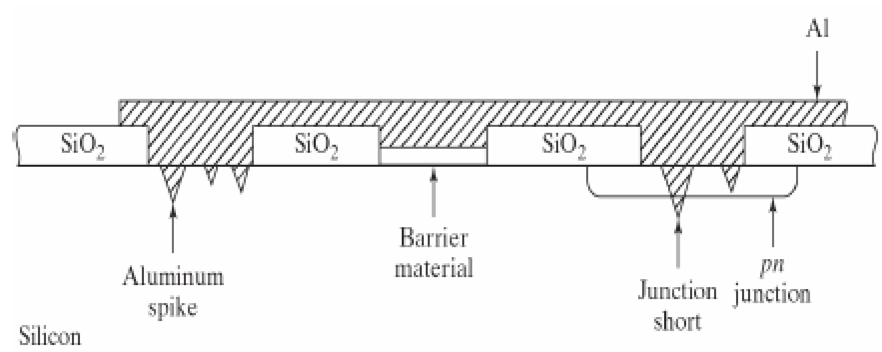
Silicon





Si particles are embedded into Al during polishing, not precipitates.

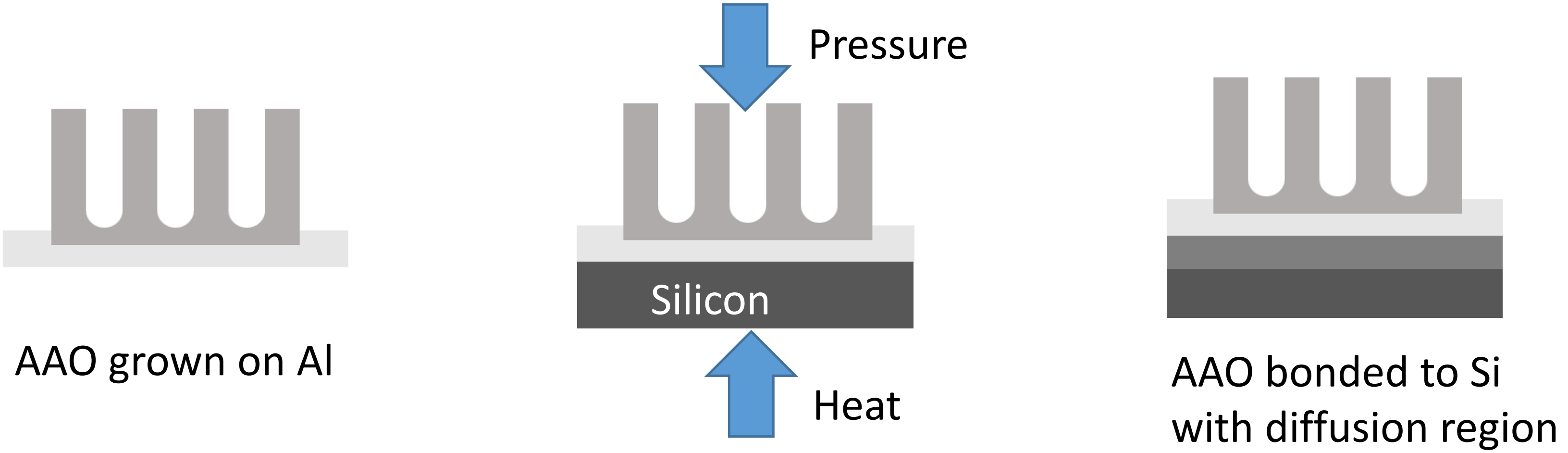
Aluminum diffusion spikes into silicon provides strong bond



Thick AAO on Si: Two Methods

- Al-Si bonding before anodization

- Al-Si bonding after anodization

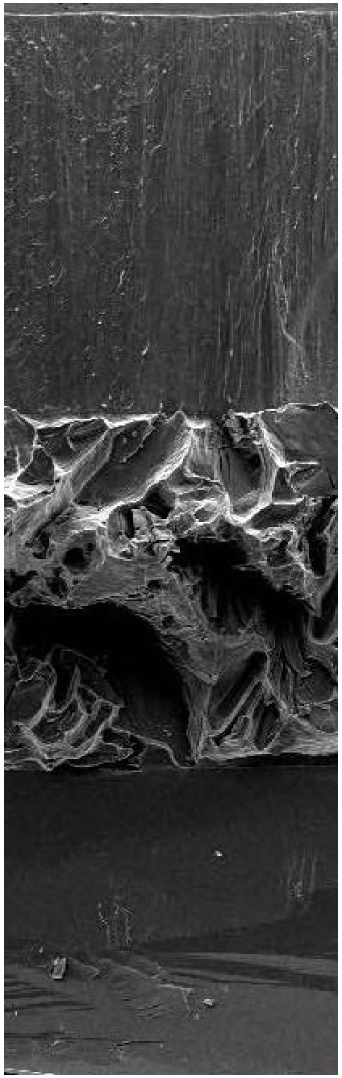


Bonding After Anodization

AAO
90 um

Aluminum
80 um

Silicon
>200 um



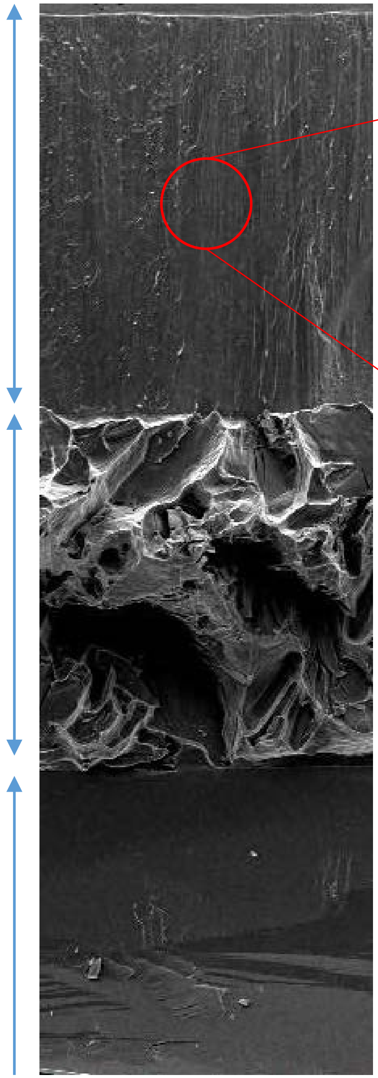
- 24 hour 1st anodization, 16 hour 2nd anodization
- 40 V, 0.3 M Oxalic acid, 15°C
- Increasing the anodization time consumes more Al and brings the AAO closer to the silicon interface.

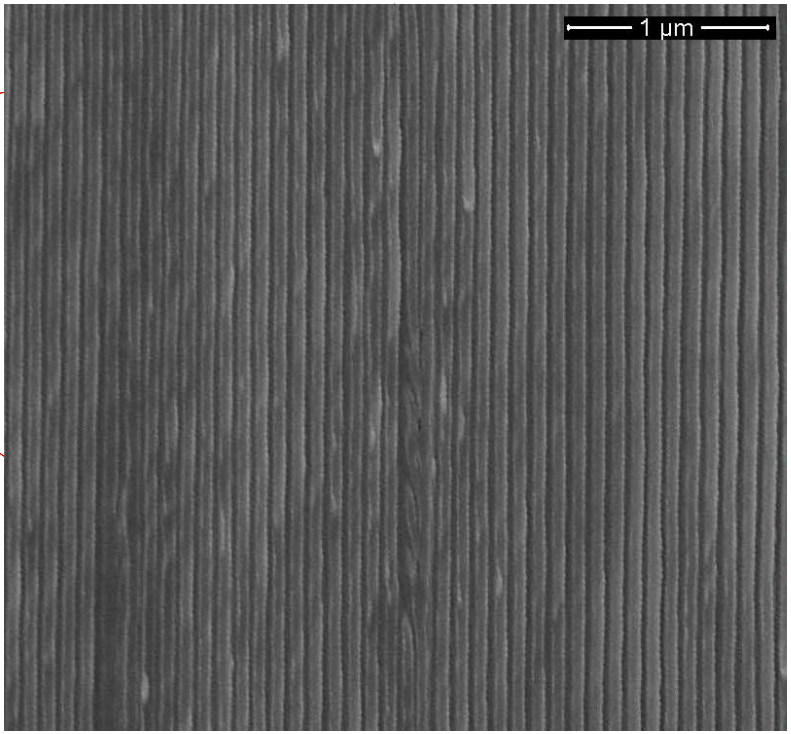
Pore Structure Unaffected

AAO
90 um

Aluminum
80 um

Silicon
>200 um





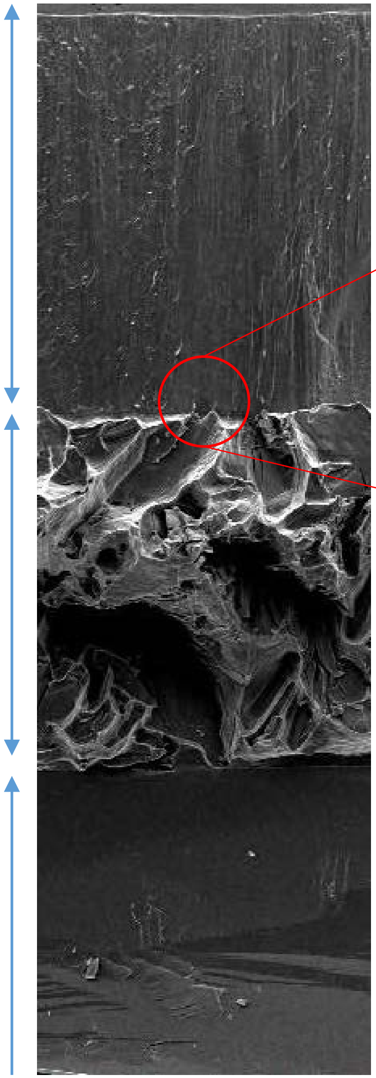
- Pore structure is undamaged through the bonding procedure.

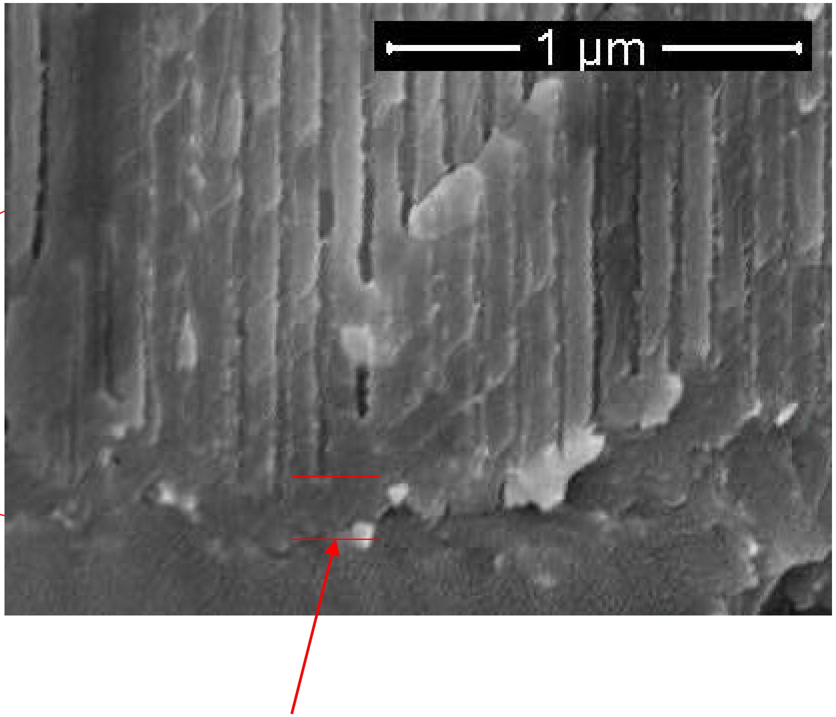
Barrier Layer Remains Intact

AAO
90 um

Aluminum
80 um

Silicon
>200 um





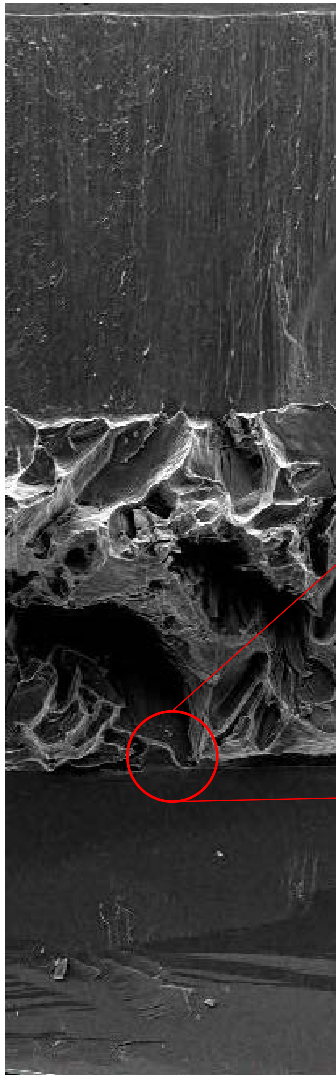
- Barrier layer at the bottom of the pores is unchanged

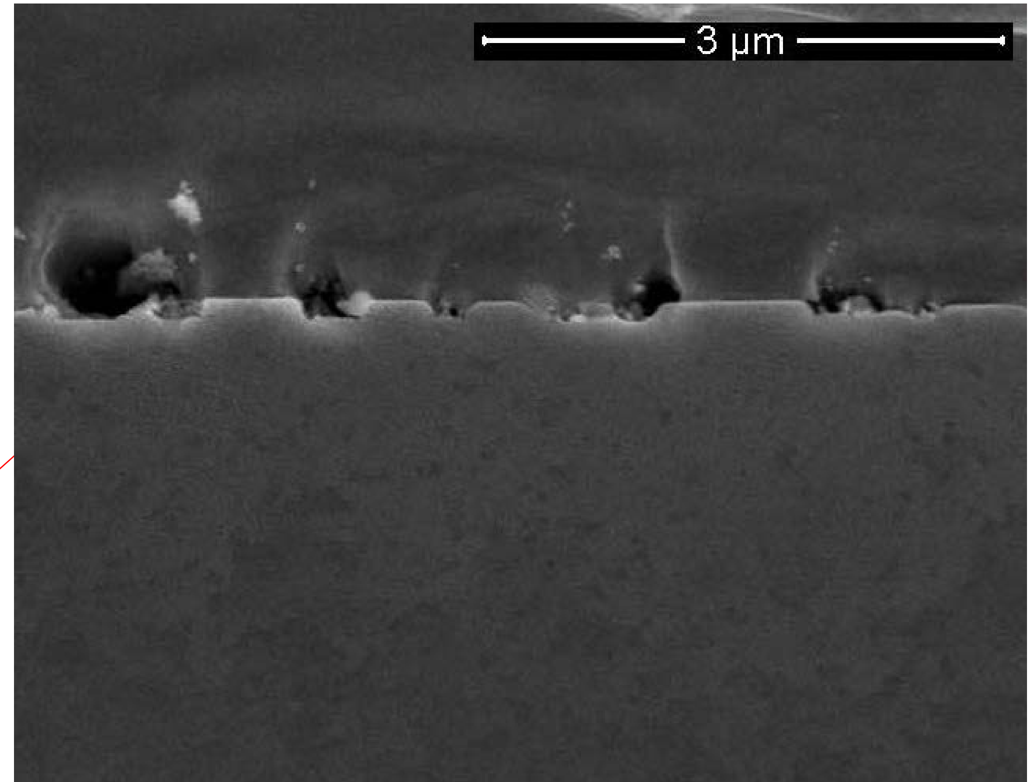
Al-Si Interface: Mixed Voids and Fusion

AAO
90 um

Aluminum
80 um

Silicon
>200 um

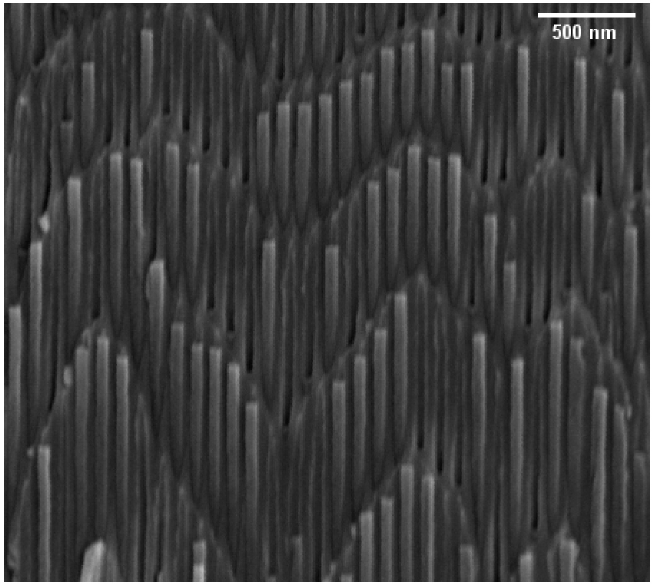




- Al-Si interface characterized by mixed voids and reaction zones.
- Perfectly planarized Al would likely decrease void content.

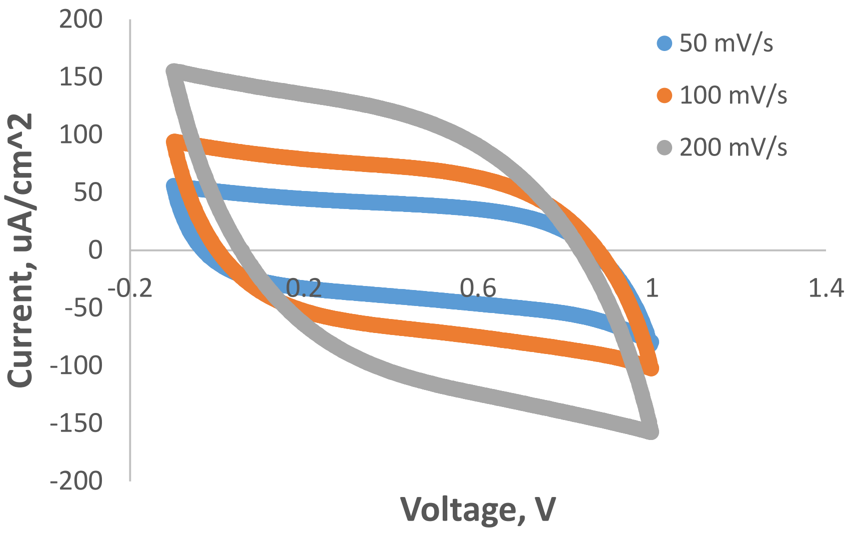
Chemical Vapor Deposition of Carbon Nanotubes in AAO-on Si

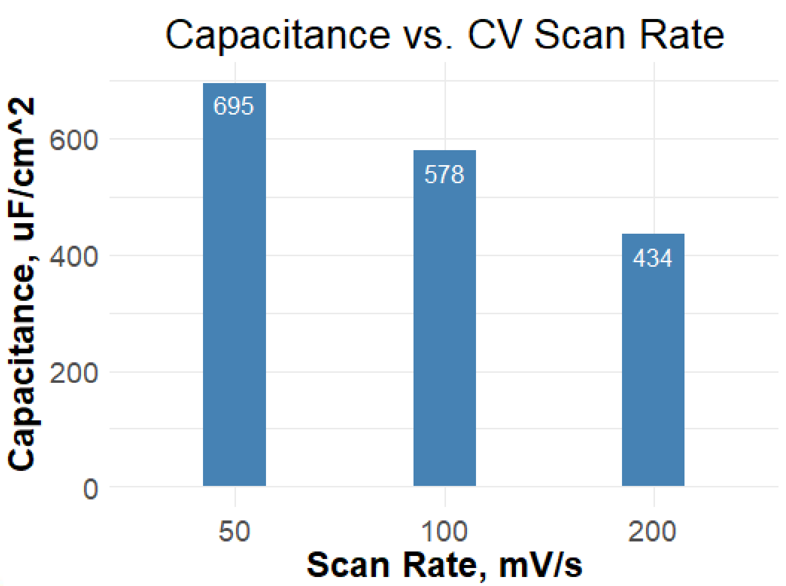
- Carbon nanotubes deposited in AAO following Ahn et al.[1]
- Bulk scale pouch cell devices were made and capacitance was calculated from cyclic voltammograms.



[1]H. J. Ahn et al., *Electrochem. commun.*, **8** (2006)

Cyclic Voltammetry Shows Promising Capacitance





- Voltage range: -0.1 – 1 V
- Sweep rate: 50 – 200 mV/s
- Maximum capacitance of 695 uF/cm^2 based on planar area

Conclusion

- Simple pressurized heat treatments offer a viable solution to producing thick templates of AAO bonded to silicon.
- Bonding either before or after anodization is possible allowing for great flexibility in nanomanufacturing.
- Thick AAO-on-Si offers a viable platform for on-chip supercapacitors with as much as 695 uF/cm^2 or more based on planar silicon area.

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14. ABSTRACT
There is a great interest to grow AAO templates directly on silicon as a carrier wafer, however most attempts rely on film deposition techniques that are generally suited for depositions on the order of 1 μm. Thicker aluminum films are desirable in order to achieve better ordering of the AAO pores through two-step anodization and for greater aspect ratio for applications where surface area is the dominant factor such as solar cell and supercapacitor devices. Here, AlSi alloys are used as adhesion layers between aluminum foils and silicon wafers as a solution to the thin film problem. High purity aluminum foils and silicon wafers are pressed together as a diffusion couple. The couple is then annealed under argon atmosphere at temperatures from 550ºC to 650ºC (from below the AlSi eutectic temperature of 577ºC to just below the Al melting temperature of 660ºC) for various times. Cross sections of these couples are examined under scanning electron microscopy (SEM) to determine the thickness of the diffusion region and to check for the presence of voids. Bonded Al-AlSi-Si composites are anodized in oxalic acid using a two-step process, and the final AAO morphology is examined under SEM.

15. SUBJECT TERMS
AAO(anodized aluminum oxide), thick film, supercapacitor, CNT(carbon nanotubes)

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